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Fe(III) BIOREDUCTION IN A KAOLIN SUSPENSION IN STORAGE

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The removal of iron from kaolin becomes more effective when bioreduction of the iron is added to the technological process. The process can be accelerated by combining as factors the moisture and temperature of the suspension, the pH–Eh of the medium, the composition of the nutrient medium, and the seeding material from a community of microorganisms. In a stagnant moisture regime of a kaolin suspension iron bioreduction is accompanied by the formation of Fe(II)–Fe(III)-containing minerals, and as a result the reduction process stops.

Key words: bioreduction, iron, green rust, magnetite, kaolin color, aerobic and anaerobic microorganisms, redox potential.

Bioleaching of iron from kaolin holds considerable promise because there exists a wide spectrum of microorganisms capable of effectuating iron bioreduction [1 – 6].

The main difference between microorganisms in terms of dissolving iron is that either their cells absorb iron (assimilation) or dissolve iron (dissimulation) with or without preliminary reduction of the iron. The assimilation of iron by an organism is of limited interest for leaching iron from kaolin because iron remains linked with the organism and does not become concentrated in large quantities in the microorganisms [2]. The simplest method of iron dissimilation is to use organic acids that dissolve iron compounds [3].

Aerobic microorganisms and fungi producing organic acids afford a relatively simple mechanism for dissolving and removing iron. However, they may not have a direct biological need to dissolve impurity iron because for them this process is secondary to feeding and obtaining energy [1]. In addition, there are limitations to using them. First and foremost, aerobic conditions must be maintained in the medium; second, the consumption of large amounts of sugar per unit dissolved iron is required; and, third, such microorganisms do not necessarily change the state of the oxidized iron in the kaolin composition, which makes the removal of iron from the kaolin less effective [4, 5].

The use of dissimilation iron-reducing organisms is more promising because they make it possible to reduce Fe(III) as well as dissolve impurity iron. From the standpoint of practicability the process of microbiological removal of iron from kaolin is more easily implemented with anaerobic iron-reducing microorganisms, which use Fe(III) as electron acceptors in respiration [6]. Bioreduction by anaerobic bacteria makes it possible to avoid the need for feeding air and mixing; in addition, it is very important to reduce the concentration of sugar in the nutrient medium.

For large-scale industrial adoption of iron-reducing operations performed on a large volume of kaolin, it is entirely possible to use definite strains of microorganisms possessing iron-reducing bioleaching capabilities. But, unfortunately, the need to maintain the purity of the cultures of the microorganisms introduced complicates the technological process of removing iron [1]. Since iron-reducing microorganisms are common in the environment [6], the most practical variant is to use naturally occurring microorganisms separated beforehand from natural sources, which have already adapted to local conditions [7, 8]. To support the development of natural types of microorganisms participating in iron reduction there is no need to sterilize the initial raw material (sterilization is an expensive process and unrealistic under production conditions). Such organisms can be found in anaerobic media, where there is no oxygen and the content of nitrogen and sulfates is low but Fe(III) minerals are present [6]. Such a medium exists at the bottom of lakes and marshes and in water-saturated layers in deposits of clays and kaolins.

At the same time it is apparent that if it becomes necessary to control the vital activity of microorganisms under na-

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tural living conditions, then a set of biotechnological conditions securing the active vital functions of an anaerobic community of iron reducing microorganisms will have to be worked out.

The aims of the present work are to establish the influence of the natural composition of the microflora of kaolin on the process of iron bioreduction in the presence or absence of a nutrient medium and to determine the influence of iron bioreduction on the transformation of iron minerals in a kaolin suspension in storage. Our tasks included the following: prove experimentally that the process of iron bioreduction in kaolin is due to the vital activity of microorganisms upon the introduction of the components of the nutrient medium and during storage; obtain stable active cenoses (communities of microorganisms) and use them as seeding material to intensify the bioreduction process; determine the main groups of microorganisms participating in this process; prove experimentally that the natural microflora of kaolin does not interfere with the development of the cenosis introduced (the composition of the cenosis is stable and is restored with repeat seeding).

MATERIALS AND METHODS OF INVESTIGATION

The object of investigation was kaolin (Prosyanovskoe deposit) with the following chemical composition (mass fraction, %): SiO_2 — 46.83; Al_2O_3 — 36.09; TiO_2 — 0.53; Fe_2O_3 — 0.81; CaO — 1.18; MgO — 0.40; K_2O — 0.88; Na_2O — 0.17; calcination losses — 13.11.

Suspension preparation conditions. The kaolin suspension with moisture content 60% was mixed for 1.0 – 1.5 h to constant hydrometric density in a ball mill (kaolin mass and milling bodies in the ratio 1 : 2). The mixture was passed through a No. 02 sieve and an SM-15 high-gradient magnetic separator and then poured into a glass vessel. Additives — the nutrient medium and the inoculum (seeding material) — were introduced into the prepared suspension as required for the preparation of the suspension of Prosyanovskoe kaolin (Table 1).

Ashby's medium was used as the nutrient medium [8]. The seeding material comprised a stable cenosis of aerobic and anaerobic microorganisms separated beforehand from Prosyanovskoe kaolin and maintained by repeated seeding on the kaolin suspension enriched with Ashby's nutrient medium.

The glass vessels with the control and experimental suspensions were stored in a thermostat at 25°C for 30 days (aging process).

Four variants of the kaolin suspensions were prepared to study the influence of microorganisms on the bioreduction of the iron in kaolin:

1) nonsterile suspension of kaolin (control sample, index CS);

2) sterile suspension of kaolin with the addition of a sterile nutrient medium (index KS);

TABLE 1. Preparation Conditions and Composition of Experimental Kaolin Suspensions

Components and preparation conditions	Variants and composition			
	1	2	3	4
Sterilization of kaolin	–	+	–	–
Modified Ashby medium, ml/kg	–	250.0	250.0	250.0
Seeding material, g/liter	–	–	–	10.0

3) nonsterile suspension of kaolin with the addition of a sterile nutrient medium (KNNM);

4) nonsterile suspension of kaolin with the addition of a nutrient medium and seeding material, containing a stable cenosis of aerobic and nonaerobic bacteria, separated beforehand from Prosyanovskoe kaolin (KNNB).

The possible influence of organic substances and other components introduced into the suspension together with the nutrient medium can be determined by comparing the CS and KS suspensions. Since the growth of microorganisms in a KS suspension is prevented by sterilization of the kaolin suspension and the nutrient medium, it serves as a control with respect to the KNNM and KNNB suspensions.

Conditions favorable for the growth of the kaolin organisms are created in the KNNM suspension. The intrinsic microorganisms and the microorganisms introduced with the seeding material underwent growth in the KNNB suspension.

Methods of investigation. The chemical composition of kaolin was determined with the use of an SMR-25 x-ray fluorescence spectrometer. For diagnostics of the iron present in the kaolin and the structural state of the iron the oxalate-soluble iron Fe_{ox} was determined by means of Tamm's reagent [8].

A pH-150 M pH meter and a set of electrodes were used to measure the pH and Eh of the kaolin suspension in the presence of natural moisture in the interior levels of the vessel. An equation presented in [8] was used to calculate the value showing the activity *pe* of the electrons in the suspension:

$$pe = \text{Eh} : 58,$$

where Eh is the redox potential in mV.

The combined redox potential [7], which takes account of the protons (pH) and the electrons (*pe*), viz., rH = 2 (*pe* + pH), was used to determine the redox state of the kaolin suspension.

A KLY-2 kappameter was used to measure the magnetic susceptibility χ, and the procedure described in [8] was used to determine the reduction capacity.

The reflection spectra of a kaolin suspension and kaolin were measured with a Pul'sar spectrocolorimeter. The colorimetric characteristics were determined in the CIE coordinates $L^*a^*b^*$, two axes of which characterize the chromaticity: the a^* axis — red ($+a^*$) and green ($-a^*$), the b^* axis —

TABLE 2. Eh and pH Change in a Kaolin Suspension in Storage

Suspension index	Storage period, days								
	1			7			30		
	pH	Eh	*pe*	pH	Eh	*pe*	pH	Eh	*pe*
CS	7.5	+480	8.3	7.0	+470	8.1	7.0	+460	7.9
KS	7.6	+490	8.4	7.5	+450	7.8	6.8	+400	6.9
KNNM	7.3	+464	8.0	7.0	+315	5.4	7.7	+140	2.4
KNNB	6.5	+462	8.0	7.45	+80	1.4	7.6	+55	0.9

yellow ($+b^*$) and blue ($-b^*$); the axis perpendicular to the chromaticity plane (the coordinates a^* and b^*) determines the luminance L^* (from 0 to 100); C^*_{ab} is the saturation; and, h_{ab} is the color tone [7, 8].

The degree of yellowness G (ASTM E 313) was evaluated by means of the indices [8]

$$G = ((1.28X - 1.06Z)/Y) \times 100,$$

where X, Y, and Z are the 1931 CIE color coordinates.

Enumeration of the microorganisms. The method of limiting 10-fold dilutions was used to enumerate the main physiological groups of microorganisms. The following media were used: beef-extract broth in 1 : 10 dilution for aerobic microflora; Vinogradskii's agar medium for bacteria; Postgate's medium with lactate for sulfate-reducing bacteria; and, Guilty's medium without asparagine for denitrifying bacteria.

RESULTS AND DISCUSSION

Change in the redox potential of the medium in suspensions of Prosyanovskoe kaolin. Redox reactions are characterized by a definite range of values of pH–Eh of the kaolin suspension medium. The main chemical elements participating in the redox reactions in a kaolin suspension are O, S, and Fe as well as C, N, and P as elements introduced with the nutrient medium. According to the calculations of the activity of electron in reducing reactions of the elements in a neutral medium (pH ~ 7), the critical values of *pe*, which for the iron reducing reactions are *pe* ~ 1.9, were obtained [9].

No significant changes in the pH were obtained during storage, with the exception of a KNNB kaolin suspension to which seeding material was added together with the nutrient medium (Table 2). The pH of this suspension in the first few days decreased from 7.3 – 7.5 to 6.5 and subsequently increased to 7.45 – 7.60. This increase is probably due in part to the reductive dissolution of iron hydroxide according to the reaction [9]

$$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O.$$

Protons are consumed in the dissolution of one mole of iron hydroxide, which, therefore, results in a reduction of the activity of protons in the KNNB kaolin suspension.

The Eh values of the control suspensions CS and KS in storage were practically stable (from 400 to 490 mV) and, according to the gradation of the values of the redox potential *pe* [7], correspond to the oxidation state of the medium (*pe* from 6.9 to 8.4). A similar redox state of the medium is also characteristic for the kaolin suspensions KNNM and KNNB during the first few days of storage, after which the values of the redox potential *pe* decreased: to moderately reduced for the KNNM suspension (*pe* from 5.4 to 2.4) and to reduced for KNNB (from 1.9 to 0.9). Therefore, when only a sterilized nutrient medium is introduced into an unsterilized kaolin suspension there is clearly not enough time, equal to 30 days, for the iron reduction reactions to occur. When seeding material is introduced into a kaolin suspension together with the nutrient medium at the seventh day redox conditions favorable for the iron reduction reaction and development of a community of strictly anaerobic bacteria are created.

Development of microbial communities. It is evident from Table 3 that up to 10^8 cells/g of aerobic bacteria and $10 - 10^4$ cells/g of anaerobic bacteria are present in the kaolin used in the present work. The composition of microorganisms in the seeding material differs from the initial composition of the kaolin microorganisms by the content of anaerobic bacteria. Enumeration of the microorganisms (Table 3) showed that anaerobic sulfate-reducing (> 10^8 cells/ml) and fermentation bacteria (10^6 cells/ml) dominated in the seeding materials, but the number of aerobic heterotrophic bacteria was 10^6 cells/ml, just as in the initial kaolin.

Communities of aerobic and anaerobic bacteria did not develop in the control variants CS and KS of the suspensions. The number of aerobic bacteria in the KNNM and KNNB suspensions increases to $10^7 - 10^8$ cells/ml on the seventh day and deceases to $10^3 - 10^4$ cells/ml by the end of the storage period (on the 30th day). The number of sulfate-reducing and denitrifying bacteria as well as bacteria with a fermentation-type metabolism increased continually to the end of the storage period, but especially actively during the first seven days. The introduction of seeding material into the kaolin suspension KNNB during the first seven days

TABLE 3. Enumeration of the Microorganisms in Kaolin

Suspension material and index	Storage time, days	Aerobic heterotrophic bacteria, cells/ml	Anaerobic bacteria, cells/ml		
			denitrifying	fermentation	sulfate-reducing
Seeding material (inoculum)	–	10^6	Not found	10^6	10^8
CS	1 – 30	10^8	10^4	10	10
KS	1 – 30	Not found	Not found	Not found	Not found
KNNM	1	10^8	10^4	10	10
	7	10^7	10^8	10^4	10^2
	30	10^3	10^8	10^6	10^7
KNNB	7	10^8	10^4	10^4	$10^6 > 10^9$
	30	10^4	10^8	10^7	

intensifies the development of strictly anaerobic bacteria – sulfate reducers and bacteria with a fermentation-type metabolism but somewhat retards the growth of denitrifiers. By the end of the storage period (on the 30th day) the number of sulfate-reducing bacteria, denitrifiers, and bacteria with fermentation-type metabolism in the KNNM and KNNB suspensions increases, reaching $10^7 – 10^9$, $> 10^8$, and $10^6 – 10^7$ cells/ml, respectively.

In summary, the introduction of a modified Ashby nutrient medium into a kaolin suspension, especially in combination with the seeding material, stimulated in the first place the development of a numerically dominant group of anaerobic bacteria. The kinetics of the number of anaerobic bacteria replacing aerobic bacteria in the kaolin suspensions KNNM and KNNB is interconnected with the formation of the reducing state of the medium.

Under the reducing conditions of the medium the reduction of Fe(III) and the synthesis of new iron minerals can be accomplished by different groups of microorganisms: on the on hand by the dissimilation iron-reducing bacteria using Fe(III) as an electron acceptor (iron-reducers, sulfate-reducing, heterotrophic bacteria, and others) and on the other hand by microorganisms giving rise to indirect reduction of Fe(III) by the products of metabolism (sulfate-reducing, aerobic heterotrophic and bacteria with fermentation-type of metabolism). In [10] it is noted that there exists a metabolic universality of microorganisms and their use of many mechanisms of iron reduction.

Color change of a kaolin suspension and transformation of iron compounds. The color characteristics were used to identify the process of bioreduction of the iron present in a kaolin suspension in storage.

During storage of the CS and KS suspensions no change in color occurred, in contrast to the KNNB suspension whose color changed gradually from light-yellow to dark green-azure. It was seen visually that the development of a characteristic dark color starts in the bottom layers of the kaolin suspension in individual microzones, in which appear small dark spots probably due to the accumulation of cells of iron-reducing bacteria and iron reduction. Then, the diameter of the colored zones gradually increased and spread to the entire mass of the suspension with the formation of a thin bright layer at the top of the kaolin suspension.

An organoleptic evaluation of the color of kaolin suspensions fully corresponds to the values of the instrumental color characteristics. Samples for measuring the reflection spectrum followed by a calculation of the color coordinates in the CIE system $L^*a^*b^*$ were obtained from the inner layer before and after storage (Table 4). Analysis of the color coordinates of the suspensions CS and KNNB makes it possible to draw the following

– during the first few days the color coordinates CIE $L^*a^*b^*$ of the suspensions are practically identical: at high lu-

TABLE 4. Change in the Color of the Control and Experimental Kaolin Samples in Storage

Suspension index and storage time	Color coordinates					G
	L^*	a^*	b^*	C^*_{ab}	h_{ab}	
Inner layer of CS suspension:						
1 day	80.89	0.60	16.05	16.06	87.82	33.56
30 days	80.52	0.63	16.15	16.08	87.36	33.40
Inner layer of KNNB suspension:						
1 day	80.89	0.60	16.05	16.06	87.82	33.56
30 days	55.22	–3.57	–0.79	3.65	192.60	–6.41

minance L^* ~ 80 the color tone h_{ab} ~ 87 corresponds to a reddish-yellow tone with yellow predominating (b^* ~ 16.0) over red (a^* ~ 0.6);

– the color coordinates CIE $L^*a^*b^*$ of the sample of the kaolin suspension KNNB change by the end of the storage period: the luminance corresponds to L^* ~ 55 on the achromaticity scale for grey color; color tone h_{ab} ~ 192 – bluish-green tone with negative values and redness a = –3.57 (green) and yellowness b^* = –0.79 (blue); the color saturation C^*_{ab} changes from 16.06 to 3.65 in the direction of color achromaticity. The yellowness index G of the kaolin suspension KNNB changed during storage from positive (G = 33.5) to negative (G = –6.41) values, and the color changes correspondingly from yellow to blue.

Formation of Fe(II)–Fe(III)-containing minerals. On the seventh day of storage the medium of the KNNB kaolin suspension corresponds to neutral conditions (pH ~ 7.45) and reducing state (pe ~ 1.4), which is fully conducive to the development of anaerobiosis and Fe(III) reduction with the formation of new minerals, including magnetite, vivanite, pyrite, and green rust [9]. However, except for green rust, the color of these minerals does not correspond to the color of the KNNB kaolin suspension by the end of the storage period.

The color coordinates of green rust correspond to the azure-green region in the Munsell system (5BG 6/1) [9], and magnetite has a very low luminance, which on the luminance scale L^* is closer to black with a reddish-yellow hue. The formation rate of green rust is higher than that of magnetite, and for this reason green rust is more likely to form under equal experimental conditions [1]. It has been shown [12] that the formation of green rust, in contrast to magnetite, largely depends on the density of the cells of iron-reducing bacteria.

Green rust is represented by Fe(II)–Fe(III)-hydroxides with different types of interlayer anion [13]. Green rust is formed under neutral conditions in a reducing medium (pH ~ 6.5 – 7.5) owing to the sorption of Fe^{2+} and different anions by amorphous iron hydroxide followed by solid-phase rearrangement of the lattice. In contrast to most iron (hydro)oxides the minerals of green rust, irrespective of their form, having an internal surface, are characterized by a large specific surface and, therefore, high reactivity [14] as well as instability in the presence of oxidation. The color of green rust rapidly changes from azure-green to colorless on contact with air. For this reason, after a KNNB suspension, having a blue-green color is dewatered, the dry kaolin acquires a white color with a yellowish tinge.

Ultrafine magnetite forms as a product of the biogenic dissimilation reduction of Fe(III) hydroxides owing to the solid-phase transformation of Fe(II) sorbed on the surface of amorphous Fe(III) hydroxides [6, 9]. A number of physical-chemical data attest indirectly to the formation of magnetite in the KNNB kaolin composition. In the first place, the fraction of oxalate-soluble iron Fe_{ox} increases in KNNB kaolin, which probably is an indication of the formation of magnetite, which is easily dissolved by Tamm's solution. In the second place, the formation of magnetite requires dissimilation reduction of Fe(III) hydroxides with the appearance of Fe(II) and Fe(III) sources as well as pH > 0.7, because this process requires OH groups: $2OH^- + Fe^{2+} + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O$. In the third place, after storage and dewatering of the KNNB kaolin suspension the magnetic susceptibility χ and the reducing capacity (RC) of the iron compounds of kaolin increase compared with the corresponding values of the control kaolin sample CS (104×10^{-6} versus 59×10^{-6} cm^3/g, respectively), which attests to the formation of an iron mineral with large values of χ, probably magnetite.

In summary, in a stagnant moisture regime of a kaolin suspension in storage a reducing medium forms, which promotes the reduction of Fe(III) on the one hand and sorption of Fe(II) and anions on the other by the surface of hydroxides and formation of secondary iron minerals – green rust and magnetite. As a result, further access of bacterial clays and reducing electron-shuttle compounds to the surface of iron hydroxides and bioreduction of Fe(III) iron ceases. A practical conclusion follows from this: to construct a technological scheme for a biological method of removing iron from kaolin it is necessary to combine the stagnant moisture regime with its replacement by a flushing regime.

CONCLUSIONS

Iron removal from kaolin becomes more effective when iron bioreduction is included in the technological scheme.

The intensification of the bioreduction of iron in a kaolin suspension can be accelerated by introducing into it, together with the nutrient medium, a seeding material comprised of a community of microorganisms separated from kaolin beforehand. In addition, the seeding material is already adapted to its natural living conditions and mineral composition, and to remove it there is no need to sterilize the kaolin beforehand or to maintain the purity of the cultures of microorganisms used, which makes it possible to use the seeding material for large volumes of kaolin.

After the first week of storage of a kaolin suspension into which a nutrient medium has been introduced, the form of the bacteria changes: the aerobic bacteria, which predominate numerically, are replaced by anaerobic bacteria, whose community functionally participates in iron bioreduction. In the process, the redox state of the kaolin suspension medium changes from moderately reducing to reducing, which does not correspond to the pH required to reduce Fe(III); the color of the suspension changes.

The color of a kaolin suspension at the end of the storage period was specified in CIE color coordinates $L^*a^*b^*$ and it was shown that according to the values h_{ab} ~ 192 it corresponds to a blue-green tone. After the suspension is dewatered the dry kaolin acquires a white color with a yellowish hue.

A kaolin suspension is characterized by a combination of factors: the state of the medium pH–Eh; a community of bacteria with strictly anaerobic bacteria predominating numerically; color corresponding to a blue-green tone; and, the different types and concentrations of ligands, introduced together with the nutrient medium or formed in the course of the vital activity of the microorganisms, are fully adequate for the formation of green rust as a precursor of magnetite during storage of a kaolin suspension.

However, it is necessary to take account of the fact that the bioreduction of iron in a kaolin suspension in storage in a stagnant moisture regime together with a combination of a number of factors results in the formation of Fe(II)–Fe(III)-containing minerals, as a result of which the Fe(III) reduction process stops.

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